

ARTICLES WITH DISPERSED CONDUCTIVE COATINGS

Background of the Invention

1. Field of the Invention

This invention relates to an articles that have a conductive layer and optionally a
5 light transmittance, and to methods for producing such articles.

2. Description of the Background

An anti-electrostatic resin plate that is able to release static electricity and avoid
dust adherence has been used for a clean room partition such as windows used in the clean
room. One such example is described in Japanese Laid Open Patent Publication
10 2001-62952. The resin material of this invention includes tangled fibers that would
extend at the time of article formation to provide a good conductivity. A substrate film,
where ITO (Indium Tin Oxide) or ATO (Antimony Tin Oxide) is placed on the surface, has
been known as a transparent conductive film with a surface resistivity of 10^0 to $10^5 \Omega/\square$
(Japanese Laid Open Paten Publication 2003-151358).

15 In the conventional anti-electrostatic transparent resin plate (Japanese Laid Open
Paten Publication 2001-62952), the carbon fibers bent and intertwined with each other are
buried in an anti-electrostatic layer. Therefore, the carbon fibers are not well dispersed.
The amount of the carbon fiber in the anti-electrostatic layer should be increased to a
certain level in order to achieve an adequate surface resistivity of 10^5 to $10^8 \Omega/\square$. The
20 anti-electrostatic transparent resin plate (Japanese Laid Open Paten Publication
2001-62952) mentioned can acquire an electromagnetic shield property when the amount
of the carbon fiber in the anti-electrostatic layer is further increased and the surface
resistivity decreases to $10^4 \Omega/\square$. However, the transparency of the anti-electrostatic layer
is deteriorated when the amount of the carbon fiber is increased. Thus, it is difficult to
25 acquire the practical anti-electrostatic transparent resin plate that has both good
transparency and electromagnetic shield property.

The transparent conductive film described in the Japanese Laid Open Paten
Publication 2003-151358 is formed through a batch method such as sputtering.
Therefore, it has a poor productivity and the high production cost.

30 Summary of Invention

The present invention overcomes the problems and disadvantages associated with

current strategies and designs and provides articles with conductive layers that demonstrate good conductivity, while acquiring better transparency, and to methods for forming such articles.

One embodiment of the invention is directed to articles with conductive layers
5 that can achieve good conductivity, with the same amount or less of the ultra fine conductive fiber such as conventionally available carbon fiber.

Another embodiment of the invention is directed to methods for forming articles with the conductive layers that demonstrate a good conductivity, the thickness of which is reduced to improve the transparency, which may be by reducing the amount of the ultra
10 fine conductive fiber.

Another embodiment of the invention is directed to method for forming articles with the transparent conductive layer that can be produced with low production costs.

Other embodiments and advantages of the invention are set forth in part in the description, which follows, and in part, may be obvious from this description, or may be
15 learned from the practice of the invention.

Description of the Drawings

Figure 1 is a cross-sectional view of an embodiment of the conductive article of this invention.

Figure 2A is a cross-sectional view showing the dispersion of the ultra fine conductive
20 fiber in the conductive layer of this invention, and Fig. 2B is another cross-sectional view showing the dispersion of the ultra fine conductive fiber in the conductive layer of this invention.

Figure 3 is a plan diagram of the conductive layer showing the dispersion of the ultra fine conductive fiber in the conductive layer.

25 Figure 4 is a transmission electron microscopic photograph showing the dispersion of the ultra fine conductive fiber in the conductive layer viewing from above.

Figure 5 is a scanning electron microscopic photograph showing the dispersion of the ultra fine conductive fibers in the conductive layer viewing from above.

Figure 6 is an optical microscopic photograph showing the ultra fine conductive fiber in
30 the conductive layer of the comparative example viewing from above.

Description of the Invention

As embodied and broadly described herein, the present invention is directed to articles that have conductive coatings, which may optionally be transparent, and methods of forming such articles.

One embodiment of the invention is directed to conductive articles that have
5 transparent conductive layers comprising ultra fine conductive fibers on at least one surface of a substrate. A characteristic of this invention is that the ultra fine conductive fibers are well dispersed, and yet in contact with each other, without densely concentrated.

The conductive article of this invention has a transparent conductive layer that has the ultra fine conductive fiber on at least one surface of the substrate. Another
10 characteristic of this invention is that the ultra fine conductive fibers are in contact with each other and yet dispersed so that each fiber is separated from other fibers or each bundle of the fiber, where a plurality of the fibers make a bundle, is separated from other bundles.

The carbon fiber, especially carbon nanotube is used as the ultra fine conductive
15 fiber in this invention. It is preferable that the fibers or the bundles of the fiber are in contact with each other and yet dispersed so that each fiber or bundle is separated from other fibers or bundles. It is also preferable that the surface resistivity of the article be 10^0 to $10^{11}\Omega/\square$. Also, the surface resistivity of the conductive layer is 10^0 to $10^1\Omega/\square$ and the light transmission of the light with 550nm wavelength is above 50%. The surface
20 resistivity of the conductive layer is 10^2 to $10^3\Omega/\square$ and the light transmission of the light with 550nm wavelength is above 75%. Or the surface resistivity of the conductive layer is 10^4 to $10^6\Omega/\square$ and the light transmission of the light with 550nm wavelength is above 88%, or the surface resistivity of the conductive layer is 10^7 to $10^{11}\Omega/\square$ and the light transmission of the light with 550nm wavelength is above 93%.

25 The conductive article of this invention has a transparent conductive layer made of thermo-plastic resin that has the carbon nanotube on at least one surface of the substrate made of a transparent thermo-plastic resin. Another characteristic of this invention is that the carbon nanotubes are in contact, yet dispersed so that each tube is separated from other tubes, and not densely concentrated.

30 The expression 'not densely concentrated' herein denotes that there is no significant lump of fibers with the average diameter of above $0.5\mu\text{m}$ when the conductive

layer is observed by an optical microscopy. The word 'contact' indicates the following two states; the carbon nanotubes make an actual contact with each other, or the carbon nanotubes are located close enough with a slight space between them that allows the flow of electricity. The word 'conductivity' means that the surface resistivity falls into the
5 scope of 10^0 to $10^{11}\Omega/\square$ when it is measured by JIS K 7194 (ASTM D 991) (when the resistivity is below $10^6\Omega/\square$) or JIS K 6911 (ASTM D 257) (when the resistivity is above $10^6\Omega/\square$).

The ultra fine conductive fibers in the conductive layer of the first conductive article of this invention are in contact with each other, and yet well dispersed without
10 being densely concentrated. The ultra fine conductive fibers are loosely crossing each other, which allows for the flow of electricity, leading to the excellent conductivity. Therefore, the same conductivity as that of the conventional art can be obtained with the smaller amount of the ultra fine conductive fiber, allowing the improved transparency and the thinner conductive layer. Since the fibers are not densely concentrated, the number of
15 the fibers contributing to the flow of electricity increases when the same amount of the ultra fine conductive fiber as that of the conventional art is applied, leading to the improved conductivity. Furthermore, if the carbon nanotube, which is thin and long, is used as the ultra fine conductive fiber, the contact between the fibers is further facilitated, allowing the control of the surface resistivity with the scope of 10^0 to $10^{11}\Omega/\square$. It is also
20 possible to obtain a good transparency. The article of this invention can also have the anti-electrostatic property, the conductive property, and the electromagnetic shield property.

The ultra fine conductive fibers or bundles of the fiber in another conductive article of this invention are in contact with each other, yet dispersed so that each fiber is
25 separated from other fibers or each of the bundle of fiber, where a plurality of the fibers make a bundle, is separated from other bundles. The frequency of fibers or bundles of fibers that make contact with each other increases, which allows for the flow of electricity, leading to excellent conductivity. Therefore, the same conductivity as that of the conventional art can be obtained with the smaller amount of the ultra fine conductive fiber,
30 allowing for the improved transparency and a thinner conductive layer. The improved conductivity is obtained when the same amount of the ultra fine conductive fiber as that of

the conventional art is applied, because the frequency for the fibers to make contact with each other has been increased. Furthermore, if carbon nanotubes are used as ultra fine conductive fibers, contact between the fibers is further facilitated. It is also possible to obtain the article with a good transparency and the article with the improved conductivity.

5 The article of this invention can also have the anti-electrostatic property and the electromagnetic shield property.

Various preferred embodiments of the invention may be explained by referring to figures. However, this invention is not limited to those embodiments.

Fig. 1 is a cross-sectional view of the conductive article in the plate form of an
10 embodiment of this invention. Fig. 2A is a cross-sectional view showing the dispersion of the ultra fine conductive fiber in the conductive layer. Fig. 2B is another cross-sectional view showing the dispersion of the ultra fine conductive fiber in the conductive layer. Fig. 3 is a plan diagram showing the dispersion of the ultra fine conductive fiber in the conductive layer.

15 A conductive article P has a conductive layer 2 with ultra fine conductive fibers laminated on one (upper) surface of a substrate 1 that is made of inorganic material such as synthetic resin, glass or ceramics. The conductive layer 2 can be formed both upper and bottom surfaces of the substrate 1.

The substrate 1 is made of thermo-plastic resin, the hardening resin that is
20 hardened by the application of heat, ultra-violet ray, electric beam or radioactive ray, glass, ceramics, or inorganic material. The transparent thermo-plastic resin, hardening resin, or glass is a desirable material for acquiring the transparent conductive article P. The transparent thermo-plastic resin includes, for example, olefin resin such as polyethylene, polypropylene, and ring polyolefin, vinyl resin such as polyvinylchloride,
25 polymethylmethacrylate, and polystyrene, cellulose resin such as nitrocellulose and triacetylcellulose, ester resin such as polycarbonate, polyethyleneterephthalate, polydimethylcyclohexeneterphthalate, and aromaticpolyester, ABS resin, the co-polymer and the mixture of these resins. The transparent hardening resin includes epoxy resin, polyimide resin and acrylic resin. The substrate 1 does not necessarily take the plate form,
30 but may comprise other forms as well.

The transparent resin with the light transmission of above 75%, preferably above

80%, and the haze of below 5% when the thickness of the substrate 1 is 3 mm, is especially desirable. Such resin includes ring polyolefin, polyvinylchloride, polymethylmethacrylate, polystyrene, triacetylcellulose, polycarbonate, polyethyleneterephthalate, polydimethylcyclohexeneterphthalate, co-polymer of these resins, mixture of these resins and hardening acrylic resin. Since glass has the excellent light transmission of above 95%, glass is used frequently for acquiring the transparent conductive article P.

The ease of forming, the thermo-stability and the durability against weathering of the substrate 1 made of resin mentioned above are improved when an adequate amount of plasticizer, stabilizer and ultra-violet ray absorbent are added. The substrate 1 can also be made opaque or semi-opaque by adding die or pigment. In this case, an opaque or a semi-opaque conductive article is acquired. Since the conductive layer 2 is transparent, the color of the die or pigment can be kept intact. The thickness of the substrate 1 should be determined according to the usage, but the thickness of the substrate is usually about 0.03 to 10mm.

The conductive layer 2 formed on one side of the substrate 1 is a transparent layer that has the ultra fine conductive fiber 3. The ultra fine conductive fibers 3 are in contact with each other, and yet dispersed without being densely concentrated. That is, the fibers or bundles of the fiber, where a plurality of the fibers makes a bundle, are in contact with each other and yet dispersed so that each fiber is separated from other fibers or each bundle is separated from other bundles. The fibers will be in one of the following three states when the conductive layer 2 is formed with the ultra fine conductive fiber 3 and a binder; the ultra fine conductive fibers are dispersed as described above in the binder, as shown in Fig. 2A; the ultra fine conductive fibers are dispersed as described above, with a part of the fiber is in the binder and other part of the fiber protrudes or exposes itself from the binder, as shown in Fig. 2B; or the combination of the two. That is, the ultra fine conductive fibers are dispersed as described above, where some fibers are buried in the binder as shown in Fig. 2A and a part of other fibers protrudes or exposes itself from the binder as shown in Fig. 2B.

The dispersion of the ultra fine conductive fiber 3 viewing from above is shown in Fig. 3. The ultra fine conductive fibers 3 or bundles of the fiber are in contact with

each other and yet dispersed so that each fiber or each bundle is separated from other fibers or other bundles. The fibers are not intensely intertwined so that they are not densely concentrated. The fibers are simply crossing each other, making contact with each other in or on the conductive layer 2. Since the fibers are loosely crossing,
5 spreading in a broader area compared to the case where the fibers are densely concentrated, the frequency for the ultra fine conductive fiber to make contact with each other is greater, achieving the excellent conductivity. The same frequency of the fiber contact (the density of the flow of electricity) should be acquired to achieve the same conductivity of 10^5 to $10^8 \Omega/\square$ as that of the conventional art. Since the fibers are dispersed as described
10 above, the smaller amount of the ultra fine conductive fiber allows the same frequency of the fiber contact, leading the better transparency. It is also possible to make the conductive layer thinner, achieving the even better transparency.

It is not necessary for the ultra fine conductive fibers 3 or bundles of the fiber to be completely separated from other fibers or bundles. Small lumps of fibers with
15 diameters of less than $0.5\mu\text{m}$ is acceptable.

The frequency of the fiber contact is higher in this invention than that of the conventional art when the same amount of the ultra fine conductive fiber 3 is applied to the conductive layer 2, leading to the improved conductivity.

Additionally, the conductivity can be improved even if the thickness of the
20 conductive layer 2, which has the ultra fine conductive fiber 3, is reduced to 5 to 500nm. Therefore, it is desirable to reduce the thickness of the conductive layer 2 to 5 to 500nm, preferably to 5 to 200nm.

Ultra fine carbon fiber such as carbon nanotube, carbon nanohorn, carbon nanowire, carbon nanofiber, and graphite fibril, ultra fine metal fiber such as metal
25 nanotube and metal nanowire made of platinum, gold, silver, nickel, and silicon, and ultra fine metal oxide fiber such as metal oxide nanotube or metal oxide nanowire made of zinc oxide are used for the ultra fine conductive fiber 3 in the conductive layer 2. The fiber with the diameter of 0.3 to 100nm and the length of 0.1 to $20\mu\text{m}$, especially 0.1 to $10\mu\text{m}$ is preferably used. Since the ultra fine conductive fibers 3 are dispersed, without being
30 densely concentrated, so that each fiber or bundle of the fibers is separated from other fibers or bundles, it is possible to acquire the article with the light transmission of above

50% when the surface resistivity of the conductive layer 2 is 10^0 to $10^1 \Omega/\square$ and, the light transmission of above 75%, when surface resistivity is 10^2 to $10^3 \Omega/\square$, and the light transmission of above 88% when the surface resistivity is 10^4 to $10^6 \Omega/\square$, and the light transmission of above 93% when the surface resistivity is 10^7 to $10^{11} \Omega/\square$. The light
5 transmission indicates the transmission rate of the light with 550nm wavelength measured by a spectrometer.

Carbon nanotube has a very small diameter of 0.3 to 80 μm among the ultra fine conductive fibers 3. Since the carbon nanotubes or bundles of the tube are separated from other tubes or bundles, there are very few obstacles for light transmission, achieving
10 the transparent conductive layer 2 with the light transmission of above 50%. The ultra fine conductive fibers 3 in the conductive layer 2 are in contact with each other, and yet dispersed well, without being densely concentrated, so that each fiber or bundle of the fiber is separated from other fibers or bundles, allowing the flow of electricity. Therefore, it is possible to control the surface resistivity with the scope of 10^0 to $10^{11} \Omega/\square$, when the
15 estimated content of the ultra fine conductive fiber 3 in the conductive layer 2 is 1.0 to 450mg/m². The value of the estimated content of the fiber can be obtained by following the steps described below. First, observe the conductive layer 2 by an electron microscopy, measuring the area occupied with the ultra fine conductive fiber in the plan area. Then, measure the thickness of the conductive layer. Then, multiply the value of
20 the fiber area by the thickness of the conductive layer acquired from the electro microscopic observation and the specific gravity of ultra fine conductive fiber (value 2.2, the average of 2.1 – 2.3, reported as the specific gravity of graphite is used when the ultra fine conductive fiber is made of carbon nanotube).

Here, the expression 'not densely concentrated' denotes that there is no lump of
25 fibers with the average diameter, which is the average of the longer diameter and the shorter diameter, of above 0.5 μm when the conductive layer is observed by an optical microscopy.

The carbon nanotube described above includes multi-layered carbon nanotube, which has a plurality of tubes made of carbon walls with different diameters enclosed
30 around the shared center axis and single-layered carbon nanotube, which has a single enclosed carbon wall around the center axis.

There is a plurality of tubes made of carbon walls with different diameters enclosed around the shared center axis in the multi-layered carbon nanotube. The carbon walls are configured as hexagonal stacking structure. Some multi-layered carbon nanotube has a carbon wall spiral that makes a plurality of layers. The desirable multi-layered carbon nanotube has 2 to 30 carbon wall layers. An excellent light transmission is acquired when the multi-layered carbon nanotube described above is dispersed as described above in the conductive layer. The more desirable carbon nanotube has 2 to 15 carbon wall layers. Usually, the multi-layered carbon nanotube is dispersed with each piece of the carbon nanotube separated from other pieces. However, in some cases, the 2 to 3 layered carbon nanotubes form bundles, which are dispersed as described above.

The single-layered carbon nanotube has a single enclosed carbon wall around the center axis. The carbon wall is configured as hexagonal stacking structure. The single-layered carbon nanotube is not easily dispersed piece by piece. Two or more tubes form a bundle. The bundles are not densely concentrated or intensely intertwined with each other. The bundles are simply crossing each other, making contact with each other, dispersed in or on the conductive layer. The preferable bundle of the single-layered carbon nanotube has 10 to 50 tubes.

The surface resistivity of 10^0 to $10^{11} \Omega/\square$ of the conductive article P with the conductive layer 2, where the ultra fine conductive fibers 3 are loosely crossing each other, is obtained with the excellent conductivity and the anti-electrostatic property, because the ultra fine conductive fiber 3 are loosely crossing each other, allowing the enough flow of electricity, even with the reduced thickness of 5 to 500nm for the conductive layer 2 when the estimated content of the ultra fine conductive fiber 3 in the conductive layer 2 is 1.0 to 450mg/m². Since the ultra fine conductive fiber is separated from other fibers and there is no lump, there are very few obstacles for light transmission, achieving the good transparency. The transparency is also improved, because the estimated content of the ultra fine conductive fiber 3 is reduced, as the thickness of the conductive layer 2 gets thinner.

The surface resistivity of 10^4 to $10^{11} \Omega/\square$ of the conductive layer 2 can be obtained even if the estimated content of the ultra fine conductive fiber 3 is reduced to 1.0 to

30mg/m². Also, the conductive layer 2 with the excellent transparency (the light transmission of above 88%) is acquired. Therefore, the transparent article can be acquired when transparent resin or glass is used for the substrate 1. The transparent conductive polycarbonate resin plate with the light transmission of above 78%, the haze of below 2%, and the anti-electrostatic property is obtained when the transparent polycarbonate resin with the thickness of about 3mm is used as the substrate 1.

The surface resistivity of 10² to 10³Ω/□ of the conductive layer 2 is obtained when the estimated content of the ultra fine conductive fiber 3 in the conductive layer 2 is increased to 30 to 250mg/m². Also, the transparent conductive layer 2 is acquired (the light transmission of above 75%). Therefore, the transparent article with the low resistivity can be acquired when transparent resin or glass is used for the substrate 1. The transparent conductive polycarbonate resin plate with the excellent conductive property, which has the light transmission of above 65% and the haze of below 4%, is obtained when the transparent polycarbonate resin with the thickness of about 3mm is used as the substrate 1. This resin plate also has the electromagnetic shield property.

The surface resistivity of 10⁰ to 10¹Ω/□ of the conductive layer 2 is obtained when the estimated content of the ultra fine conductive fiber 3 in the conductive layer 2 is increased to 250 to 450mg/m², while keeping the transparency of the conductive layer 2 (the light transmission of above 50%). Therefore, the transparent conductive article can be acquired when transparent resin is used for the substrate 1. The transparent conductive polycarbonate resin plate with the excellent conductive property, which has the light transmission of above 45% and the haze of below 5%, is obtained when the transparent polycarbonate resin with the thickness of about 3mm is used as the substrate 1. This resin plate also has the electromagnetic shield property. The light transmission of the conductive layer 2 can be obtained by correcting the light transmission of the light with 550nm wavelength of the article using the light transmission of the substrate. A spectrometer is used for measuring. The transmission and the haze are measured according to ASTM D 1003.

The improvement of the dispersion of the ultra fine conductive fiber 3 is important to achieve the better conductivity and transparency of the conductive layer 2 by adding a large amount of the ultra fine conductive fiber 3 to the conductive layer 2. It is

also important to form the thinner conductive layer 2 by reducing the viscosity of the coating solution. Therefore, the disperser should be used for the better dispersion. Macromolecule disperser and coupling agent such as alkylammonate solution of acid polymer, tertiary amine modified alkyl co-polymer, and co-polymer between
5 polyoxyethylene and polyoxypropylene are used as the disperser. Additive such as ultra-violet ray absorbent, surface modifier, and stabilizer can be added to the conductive layer 2 in order to achieve the durability against weathering and other properties.

The transparent thermo-plastic resin, especially polyvinylchloride, co-polymer between vinylchloride and vinyl acetate, polymethylmethacrylate, nitrocellulose,
10 chlorinated polyethylene, chlorinated polypropylene, and fluorovinylidene and the transparent hardening resin that is hardened by the application of heat, ultra-violet ray, electric beam or radioactive ray, especially melamine acrylate, urethane acrylate, epoxy resin, polyimide resin, and silicon resin such as acryl-transformer silicate are used as a binder. Therefore, the conductive layer 2, which is made of the transparent binder and
15 the ultra fine conductive fiber, is a transparent layer. Also, inorganic material such as colloidal silica can be added to the binder. When the substrate 1 is made of a transparent thermo-plastic resin, the same transparent thermo-plastic resin or the different transparent thermo-plastic resin with the mutual-solubility is preferably used as the binder for acquiring the transparent conductive article. The article P with the durability against
20 wearing can be obtained when the binder with a hardening resin or colloidal silica is used. Since the conductive layer 2 is formed on the surface of the substrate 1, adequate binder should be chosen to improve the particular property such as the durability against weathering, surface strength, and durability against wearing.

When the estimated content of the ultra fine conductive fiber 3 in the conductive
25 layer 2 is $1.0 - 450\text{mg/m}^2$, and when the thickness of the conductive layer 2 is reduced to $5 - 500\text{nm}$, the surface resistivity of 10^0 to $10^{11}\Omega/\square$ with the excellent conductivity, the anti-electrostatic property, and transparency is obtained, because the ultra fine conductive fibers 3 or the bundle of the fiber are dispersed so that each fiber or bundle is separated from other fibers or bundles. The preferable estimated content of the ultra fine
30 conductive fiber 3 is 1.0 to 200mg/m^2 and the preferable thickness of the conductive layer 2 is 5 to 200nm . The powdered conductive metal oxide of 30 to 50 weight% can be

added beside the ultra fine conductive fiber to the conductive layer 2.

The conductive article P described above can be efficiently produced, for example, by the following methods. First, the binder for forming the conductive layer is solved into a volatile solvent. The ultra fine conductive fiber 3 is equally dispersed in this
5 solution, making a coating solution, which is then applied to one surface of the substrate 1. The conductive layer 2 is obtained by drying the coating solution on the substrate 1, forming the conductive article P. In the second method, the coating solution is applied to the surface of the thermo-plastic resin film, which is the same thermo-plastic resin film as that the substrate 1 or the different thermo-plastic resin film with the mutual-solubility.
10 Then, the coating solution is dried on the conductive film, forming the conductive film with the conductive layer 2. The conductive film is placed to one surface of the substrate 1 through thermal pressing or roll pressing, forming the conductive article P. In the third method, the coating solution is applied to and dried on a peeling-off film made of polyethyleneterephthalate, forming the conductive layer 2. Then, if necessary, an adhesive
15 layer is formed on the conductive layer 2, forming a transfer film. The transfer film is pressed on one surface of the substrate 1, transferring the conductive layer 2 or the both adhesive layer and the conductive layer 2. The conductive article P is obtained. Also, the article of this invention can be produced by any conventional methods.

When the article P is formed through the first method, it is important to apply the
20 thermal pressing at the final stage of the forming, because the thermal pressing can shrink the conductive layer 2 in the vertical direction. The frequency of contact between the ultra fine conductive fibers, which are dispersed in the conductive layer 2, increases and the space between the fibers is reduced, promoting the better flow of electricity, when the conductive layer 2 is pressed down in the vertical direction. This method has an effect to
25 further reduce the surface resistivity. If the latter methods, the laminating method or transfer method is employed, the thermal pressing at the final stage of the production is not necessarily required, because the conductive layer has already been pressed down during the thermal pressing or the transferring process. Also, the final thermal pressing is not required if the desirable conductivity for the particular use of the conductive article
30 has already been achieved before its application.

The following examples illustrate embodiments of the invention, but should not be

viewed as limiting the scope of the invention.

Examples

Comparative Example 1 and Example 1

Powdered vinylchloride resin as the binder is solved into cyclohexanon used as a
5 solvent. The multi-layered carbon nanotube (product of Tsinghua-Nafine Nano-Powder
Commercialization Engineering Center, with the average outer diameter of 10nm) is added
to the solution described above with the content percentage shown in the Table 1. Also,
alkylammonate solution of acid polymer, of 10 weight% of the multi-layered carbon
nanotube is added to and equally dispersed in the solution as the disperser. Two kinds of
10 coating solution with the different content percentage of the multi-layered carbon
nanotube and the binder are acquired.

Vinylchloride resin film with the thickness of 0.1mm is used as the substrate.
The coating solution is applied to the surface of the substrate with the variety of thickness.
Then, the substrate is placed on the vinylchloride resin sheet with the thickness of 0.5mm
15 after the solution is dried and hardened. Then, the substrate is pressed in temperature of
160C° with the pressure of 30kg/cm². Six kinds of transparent conductive vinylchloride
resin sheets a – f, each of which has the conductive layer with the different content
percentage of the multi-layered carbon nanotube and the different thickness, are acquired.
Also, the vinylchloride resin sheet g for the comparative example 1 is prepared by pressing
20 the vinylchloride resin film as the substrate and the vinylchloride resin sheet together.

The light transmission, the haze and the surface resistivity are measured for each
of the transparent conductive vinylchloride resin sheets a – f and for the vinylchloride
resin sheet g for comparison. The results are listed in the Table 1. The estimated
content of the carbon nanotube of each of the resin sheets and the light transmission of the
25 light with 550nm wavelength of the conductive layer of each of the sheets are also listed in
the Table 1.

The light transmission and the haze are measured by a direct reading haze
computer HGM-2DP, a product of Suga Shikenki according to ASTM D1003. The surface
resistivity is measured by a Highlester produced by Mitsubishi Kagaku, according to
30 ASTM D 257 or measured by a Rollester produced by Mitsubishi Kagaku, according to
ASTM D991. The light transmission is measured by a Shimazu auto-recording

spectrometer UV-3100PC produced by Shimazu Seisakusho. The difference in the light transmission of the light with 550nm wavelength between the transparent conductive vinylchloride resin sheets and the vinylchloride resin sheet for comparison is recorded.

Table 1

5 The content percentage of the multi-layered carbon nanotube and the thickness are different between the resin sheets c and e, or the resin sheets d and f. However, each pair shows about the same surface resistivity, because each pair has about the same estimated content of the multi-layered carbon nanotube, as seen from the Table 1. As to the resin sheets a, b, c, and d, as the content percentage of the multi-layered carbon
10 nanotube increases from 3mg/m^2 to 20mg/m^2 , the surface resistivity decreases from $10^7 \Omega/\square$ to $10^4 \Omega/\square$, showing the improving anti-electrostatic property, and the light transmission decreases from 88% to 80%, while keeping the good transparency of above 80%. As it is obvious from this result, the surface resistivity and the light transmission decrease in proportion to the increase of the estimated content of the multi-layered carbon
15 nanotube, even though the content percentage of the multi-layered carbon nanotube and the thickness of the layer are different among the resin sheets, if the carbon nanotube is dispersed without being densely concentrated. Therefore, the estimated content of the carbon nanotube should be 3 to 20mg/m^2 in order to obtain the surface resistivity of $10^4 \Omega/\square$ to $10^7 \Omega/\square$. If the lower surface resistivity is desired, the estimated content of the
20 multi-layered carbon nanotube should be further increased. The estimated content of the multi-layered carbon nanotube can be increased either by increasing the content percentage of the carbon nanotube or increasing the thickness of the conductive layer.

There is no big difference in haze among the transparent conductive vinylchloride resin sheets a – f. The light transmission of the resin sheets a – f is lower than that of the
25 light transmission of the resin sheet g of the comparative example, by 3 to 10%. But they have the enough light transmission of above 80% for the practical use of the transparent resin sheet.

Example 2

30 The multi-layered carbon nanotube (product of Tsinghua-Nafine Nano-Powder Commercialization Engineering Center, with the average outer diameter of 10nm) and tertiary amine modified alkyl co-polymer as the disperser are added to and equally

dispersed in ethanol solvent. This coating solution is prepared such that it has 0.007 weight % of the multi-layered carbon nanotube and the 0.155 weight % of the disperser.

This coating solution is applied to the surface of a polycarbonate plate, which is a product of Takiron Co. Ltd., with the thickness of 3mm, the light transmission of 90.2%,
5 and the haze of 0.40%. The transparent conductive polycarbonate resin plate with the conductive layer of the thickness of 29nm and the estimated content of the multi-layered carbon nanotube of 2.5mg/m^2 is obtained after the solution is dried. The surface resistivity and the light transmission of the conductive layer of the resin plate are measured by the same way as that of the example 1. The surface resistivity is $3.2 \times$
10 $10^{10}\Omega/\square$, and the light transmission is 95.0%. The light transmission and the haze of the transparent conductive polycarbonate are measured by the same way as that of the example 1. The light transmission is 83.8% and the haze is 1.0%.

Example 3

1.7 weight% of the powdered vinylchloride resin as the binder is solved into
15 cyclohexanon solvent. The single-layered carbon nanotube (product of Carbon Nano Technology, with the diameter of 0.7 - 2nm) and alkylammonate solution of acid polymer, as a disperser are added to and equally dispersed in the solution. This coating solution has 0.3 weight% of single-layered carbon nanotube and 0.18 weight% of disperser. This coating solution is applied to and dried on the surface of acryl film with the thickness of
20 $100\mu\text{m}$, acquiring the conductive laminate film. The transparent conductive vinylchloride resin plate is obtained by pressing the laminate film described above to the vinylchloride resin plate with the thickness of 3mm in the temperature of 160°C with the pressure of 30Kg/cm^2 .

The conductive layer of this resin plate is observed by a transmission electron
25 microscopy (a product of Nihon Denshi Kogyo Corp., JEM-2010), measuring the area ratio of the single-layered carbon nanotube. The area ratio of the single-layered carbon nanotube is 11.1%. The thickness of the conductive layer is 65nm. Therefore, the estimated content of the single-layered carbon nanotube is 15.9mg/m^2 , acquired by multiplying the area ration 11.1% by the thickness of 65nm and the specific gravity (2.2).
30 The surface resistivity and the light transmission of the conductive layer of the resin plate are measured by the same manner as that of the example 1. The surface resistivity is 3.3

$\times 10^7 \Omega/\square$, and the light transmission is 92.8%. The light transmission and the haze of the transparent conductive vinylchloride resin plate are measured by the same way as that of the example 1. The light transmission is 80.1% and the haze is 1.6%.

Additionally, the conductive layer of the transparent conductive vinylchloride resin plate is observed by an optical microscopy (a product of Nikon Corp., OPTIPHOTO 2-POL). No lump with the size of $0.5\mu\text{m}$ is observed. Then, the conductive layer of the resin plate is observed by a transmission electron microscopy. As it is seen from Fig. 4, the single-layered carbon nanotube is dispersed well, with no lump with the size of $0.5\mu\text{m}$. Although the single layered carbon nanotubes are somewhat bent, the bundles are equally dispersed so that each bundle is separated from other bundles, and yet in contact, simply crossing each other.

Example 4

The coating solution is prepared by the following procedure. Single-layered Carbon nanotube (synthesized by referring to Chemical Physics Letters, 323 (2000) P 580 – 585, with the diameter of 1.3 – 1.8nm) and the co-polymer between poly oxy-ethylene and poly oxy-propylene as the disperser are added to and dispersed in the mixture of isopropylene alcohol and water (with the compound ratio of 3:1) as a solvent. This coating solution is prepared such that it has 0.003 weight% of single-layered carbon nanotube and 0.05 weight% of disperser. This coating solution is applied to the surface of a polyethyleneterephthalate film with the thickness of $100\mu\text{m}$ (with the light transmission of 94.5%, and the haze of 1.5%). After drying the solution, the film is coated with the urethane acrylate solution diluted to 1-600th with methyl isobutyl ketone, and then dried. The transparent conductive polyethyleneterephthalate film is obtained.

The conductive layer of the film is observed by a scanning electron microscopy (a product of Hitachi Seisakusho, S-800). The area ratio of the single-layered carbon nanotube is 70.3%. The thick ness of the conductive layer is 47nm. Therefore, the estimated content of the single-layered carbon nanotube in the conductive layer is $72.7\text{mg}/\text{m}^2$, acquired by multiplying the area ratio of 70.3% by the thickness of 47nm and the specific gravity (2.2). The surface resistivity and the light transmission of the conductive layer of the film are measured by the same method used in the example 1. The surface resistivity is $5.4 \times 10^2 \Omega/\square$ and the light transmission is 90.5%. The light

transmission and the haze of the transparent conductive polyethyleneterephthalate film are measured by the same way as that of the example 1. The light transmission is 85.8% and the haze is 1.8%.

Additionally, the conductive layer of the transparent conductive
5 polyethyleneterephthalate film is observed by an optical microscopy. No lump with the size of $0.5\mu\text{m}$ is observed. Then, the conductive layer of the film is observed by a transmission electron microscopy. As it is seen from Fig. 5, the single-layered carbon nanotube is dispersed well, with no lump. The bundles of the single-layered carbon nanotube are equally dispersed so that each bundle is separated from other bundles, and
10 yet in contact, simply crossing each other.

Example 5

The coating solution, which is used in the Example 4, is applied to and dried on the surface of a polyethyleneterephthalate film used in the Example 4, obtaining the transparent conductive polyethyleneterephthalate film with the estimated content of the
15 carbon nanotube in the conductive layer of $267.3\text{mg}/\text{m}^2$. The surface resistivity and the light transmission of the conductive layer of the film are measured by the same method used in the example 1. The surface resistivity is $8.6 \times 10^1 \Omega/\square$ and the light transmission is 60.6%. The light transmission and the haze of the transparent conductive polyethyleneterephthalate film are measured by the same way as that of the example 1.
20 The light transmission is 57.1% and the haze is 5.4%.

Comparative Example 2

1.7 weight% of the powdered vinylchloride resin as the binder is solved into cyclohexanon solvent. The single-layered carbon nanotube used in the Example 3 and aluminum-coupling agent as a coupling agent are added to and equally dispersed in the
25 solution. This coating solution has 0.3 weight% of single-layered carbon nanotube and 0.12 weight% of coupling agent. This coating solution is applied to and dried on the surface of acryl film, as in the Example 3, acquiring the conductive laminate film. The transparent vinylchloride resin plate is obtained by pressing the laminate film described above to the surface of the vinylchloride resin plate.

30 The conductive layer of the film is observed by a transmission electron microscopy. The area ratio of the carbon nanotube is 12.0%. The thickness of the

conductive layer is 62nm. Therefore, the estimated content of the carbon nanotube in the conductive layer is 16.4mg/m^2 , acquired by multiplying the area ration 12.0% by the thickness of 62nm and the specific gravity (2.2). The surface resistivity and the light transmission of the conductive layer are measured by the same method used in the example 1. The surface resistivity is $2.2 \times 10^{10}\Omega/\square$ and the light transmission is 92.5%. Although the estimated content of the carbon nanotube and the light transmission are almost the same as those of the Example 3, the surface resistivity is higher by $10^3\Omega/\square$.

The conductive layer of the resin plate is observed by an optical microscopy. As it is seen from Fig. 6, the carbon nanotube is not dispersed enough and there are pluralities of lumps. The lumps with the size of $0.5\mu\text{m}$ are observed. The biggest size of the lump reaches $10\mu\text{m}$. The large difference in the surface resistivity between the Example 3 and the Comparative Example 2 is due to the presence of the lump of the carbon nanotube. That is, the Example 3 has the excellent surface resistivity because there is no lump of the carbon nanotube. The carbon nanotubes or bundle of the tube are dispersed in the conductive layer or on the surface of the conductive layer so that each tube or bundle are separated from other tubes or bundles, and yet simply crossing each other in the Example 3. The loosely crossing carbon nanotubes are present in a broader area, increasing the frequency of contact between the carbon nanotubes. As a result, the improved conductivity is acquired.

Other embodiments and uses of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. All references cited herein, including all publications, U.S. and foreign patents and patent applications, are specifically and entirely incorporated by reference. It is intended that the specification and examples be considered exemplary only with the true scope and spirit of the invention indicated by the following claims.

Table 1

No	layer components (Wt%)			thickness (nm)	CNT content (mg/m ²)	regivity (Ω/\square)	resin sheet		layer
	CNT	disperser	binder				total transmission (%)	phase (%)	
a	20	2	78	11	3.2	1.21×10^7	87.8	1.0	97.2
b	20	2	78	21	6.5	1.73×10^6	86.4	0.9	96.0
c	20	2	78	32	9.8	2.89×10^5	85.2	0.9	-
d	20	2	78	65	20.0	4.51×10^4	79.5	0.9	88.7
e	60	6	34	9	9.7	1.03×10^5	85.5	0.8	-
f	60	6	34	19	19.5	7.77×10^4	80.6	1.0	89.8
g	-	-	-	-	-	$>10^{14}$	90.8	1.3	-

CNT: Multi-wall carbon nanotubes